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Development of new pH-adjusted fluorogypsum-cement-fly ash blends: Preliminary investigation of strength and durability properties

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HIGHLIGHTS

- New fluorogypsum-fly ash-Portland cement blend for outdoor/underwater construction.
- Preliminary investigation of strength and durability properties.
- Investigation of effects of different compositions.
- Other relevant properties investigated for a promising composition.
- Identified promising compositions for outdoor/underwater applications.

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ABSTRACT

This paper develops a new low-cost construction material made of pH-adjusted fluorogypsum, class C fly ash, and type II Portland cement. The proposed fluorogypsum-based blend is durable in water and has a lower weight and lower cost than ordinary concrete. A preliminary investigation of strength and durability properties of this new construction material is also presented. A series of compressive strength tests and volumetric expansion measurements were conducted on specimens after 28 days of curing. The experimental results were used to develop response surface models. These models can be used to predict accurately compressive strength and volumetric expansion as functions of the relative content, in dry weight, of different components. The response surface models were employed to determine ranges of dry components of the system with sufficient strength and limited volumetric expansion. A composition with 62% pH-adjusted fluorogypsum, 35% fly ash, and 3% Portland cement was selected based on strength and volumetric expansion properties to conduct additional experimental studies to quantify its modulus of elasticity, Poisson's ratio, setting times, density, void contents, and curing time effects on strength and volumetric expansion. The investigation results suggest that the proposed fluorogypsum-based blend is a promising low-cost concrete-like material for use in outdoor and underwater construction applications.

1. Introduction

Millions of tons of solid by-product materials are generated by industrial processes throughout the world every year and are accumulated over time in landfills. This large accumulation of industrial by-products represents a significant environmental hazard, produces substantial costs to public organizations and private companies, and generates significant economic and social losses [1]. The use of solid industrial by-products in the construction industry has received significant attention due to the large worldwide demand of construction materials starting from the late 1970s [2–4]. In particular, the following benefits of using by-product materials in construction have been identified: (1) reduction of construction costs [5]; (2) reduction of construction carbon footprint [6,7]; (3) limitation of undesirable environmental impacts by reducing the amount of by-products introduced in the environment [8]; and (4) reduc-

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tion of the land loss caused by the disposal of these by-product materials [8].

Among these industrial by-products, several types of gypsum materials are used for different applications in the construction industry [9]. This study focuses on the use of fluorogypsum (FG) for outdoor and underwater construction applications. FG is an acidic by-product generated during the industrial production of hydrofluoric acid (HF) from fluorspar. FG is discharged in the form of slurry into a holding pond until it becomes a solidified dry residue with low pH after water evaporation [10]. The total consumption of fluorspar in US was 601,000 metric tons in 2001; 60–65% of this consumption (i.e., 376,000 metric tons) was used to produce HF [11]. Based on the chemical reaction for HF production, i.e.,

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4 \quad (1)$$

the production of FG in 2001 can be estimated as about 660,000 metric tons [12]. The 2015 production capacity of FG in Louisiana alone was about 360,000 metric tons (G. Mitchell, Brown Industries, personal communication, 2015). Before use, the dry FG is removed from the holding pond, mixed with 2%–5% of alkali materials such as lime or circulating fluidized bed combustion (CFBC) ash [13], crushed and screened to obtain a pH-adjusted, well-graded sandy silt material with gravel size grains [10], referred to as pH-adjusted FG hereinafter. The pH-adjusted FG has pH $\approx$ 7 due to the reaction of the alkali materials with the residual sulfuric acid in the slurry FG.

Blends of pH-adjusted FG with other cementitious materials (e.g., Portland cement, fly ash, lime, and/or ground granulated blast furnace slag) have recently attracted the attention of researchers for use as pavement base materials [14–16], as a non-structural plaster for indoor applications, and as a structural material for outdoor applications [17]. However, to the knowledge of the authors, the use of FG-based blends in underwater applications has not been considered in the literature, most likely due to their relatively long setting time [17] and to the durability issues caused by the moderate solubility of gypsum materials in water, which can dramatically decrease the mechanical strength of gypsum-based blends [18]. The research presented in this manuscript is the first preliminary investigation on the strength and durability properties of pH-adjusted FG-cement-fly ash blends in order to determine the feasibility of their usage for outdoor and underwater applications.

2. Research objective, needs, and relevance

The objective of this paper is to develop a low-cost FG-based blend that can be used as a construction material for outdoor and underwater applications. The proposed blend is made of: (1) pH-adjusted FG, (2) class C fly ash (FA), and (3) type II Portland cement (PC). In this study, the pH-adjusted FG material is utilized as provided by the producer, i.e., it already contains 2%–5% CFBC ash and it is not further processed to modify and/or improve its characteristics before its use as a component of the FG-based blends. As such, the resulting blend contains grains of a 2 cm maximum diameter. These grains of pH-adjusted FG effectively behave as coarse aggregate and the resulting FG-based blend can be considered a concrete system, in which the binder consists of the mix of fine pH-adjusted FG, FA, and PC. It is also noteworthy that the investigation presented in this paper aims to develop an FG-based blend that can be used as a direct low-cost substitute for Portland cement concrete and/or crushed limestone in a variety of outdoor and underwater applications.

Utilization of FG-based blends can potentially present some important advantages over the usage of Portland cement concrete in outdoor construction applications and of limestone in road base and underwater applications, e.g.: (1) lower unit weight of the blend (with values contained between 70% and 92% of the concrete unit weight, see [17]) and, thus, lighter structures; (2) lower cost of production, e.g., FG-based blends contain only small amounts of Portland cement (i.e., less than 10% in weight of the dry components) and have a considerably lower cost than ordinary concrete [21]; (3) lower carbon footprint, e.g., due to the lower amounts of Portland cement in FG-based blends than in ordinary concrete; and (4) wider availability of pH-adjusted FG in US coastal regions where aggregate for concrete or limestone is not readily available [22,23]. However, additional understanding of the physical, chemical, and mechanical behavior of FG-based blends is needed to develop a material that can be reliably used for outdoor and underwater construction applications. This understanding is a crucial prerequisite to determine the feasibility of FG-based blends, identify additional research needs, and support future development of this type of material.

In this work, strength and durability properties of FG-based blends made of different amounts of pH-adjusted FG, PC, and FA are investigated. Two response surface models (RSMs) are developed for the prediction of compressive strength and volumetric expansion for different FG-based compositions after 28 days of wet curing (i.e., at 100% humidity). Additional mechanical and physical properties that are relevant for construction applications (i.e., setting time, void content, modulus of elasticity, and Poisson's ratio) are investigated for a select composition that appears to be particularly promising (based on strength, volumetric expansion, and cost considerations) for outdoor and underwater construction applications. For this composition, curing time-compressive strength and curing time-volumetric expansion relationships are also proposed. The study presented in this paper is part of a wider research effort to demonstrate the feasibility and improve the performance of FG-based blends for outdoor and underwater construction applications [19,20,24]. Investigation of the water solubility of these blends is a major component of this effort [24], but it is out of the scope of the present paper.

3. Dependence of strength and volumetric expansion on composition

In this study, compressive strength and volumetric expansion were considered as the critical parameters to identify appropriate composition ranges of FG-based blends for outdoor/underwater applications. In fact, compressive strength is a crucial mechanical property that controls the load-carrying capacity of a structural material. The volumetric expansion, which generally occurs due to delayed formation of ettringite [25,16], is an important property related to the durability of the material and is commonly associated with significant strength deterioration and even integrity loss due to formations of cracks inside the blend, and with potential damage to adjacent materials. However, the expansion of a blend could also be a useful property for some specific applications, e.g., expansive concrete can be used to compensate for drying shrinkage [26]. In this study, the focus is on short-term properties of the material and, thus, only expansion during curing is considered, whereas expansion under prolonged water immersion, albeit important, was considered out of the scope of the paper. It is noteworthy that internal and/or invisible cracks can also have an important effect on the mechanical properties and the durability of the material under consideration. However, since they are more complex to investigate than visible cracks, they were also deemed out of the scope of this investigation on strength and durability of FG-based blends, considering its preliminary nature. This section of the paper describes the methodology followed to investigate these properties and illustrates the results of the investigation.